

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number
WO 03/000960 A1

(51) International Patent Classification⁷: **C25C 7/06**,
G01R 31/02

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(21) International Application Number: **PCT/FI02/00522**

(84) Designated States (regional): Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(22) International Filing Date: 14 June 2002 (14.06.2002)

Declarations under Rule 4.17:

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:
20011351 25 June 2001 (25.06.2001) FI

(71) Applicant (for all designated States except US): **OUTOKUMPU OYJ [FI/FI]**; Riihitontuntie 7, FI-02200 Espoo (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **RANTALA, Ari [FI/FI]**; Vehnätie 2 A 2, FIN-06400 Porvoo (FI). **VIRTANEN, Henri [FI/FI]**; Liikastentie 99, FIN-28610 Pori (FI).

(74) Agent: **OUTOKUMPU OYJ**; Intellectual Property Management, P.O. Box 27, FIN-02201 Espoo (FI).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR)

— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/000960 A1

(54) Title: METHOD FOR THE IMPROVEMENT OF CURRENT EFFICIENCY IN ELECTROLYSIS

(57) Abstract: The invention relates to a method for the improvement of current efficiency in electrolysis. According to the method, a theoretical cell voltage is first calculated, which is compared with the measured voltage. The cumulative difference between the theoretical and measured cell voltage is monitored constantly and when this difference is proportioned to the current efficiency, information on the status of the process can be obtained continually. A decrease in current efficiency is a clear indicator of short circuits between the electrodes, and by means of the method according to the invention, it is possible to concentrate the short circuit removal work onto the correct cell groups, from the point of view of the current efficiency of the electrolysis.

METHOD FOR THE IMPROVEMENT OF CURRENT EFFICIENCY IN ELECTROLYSIS

5 The invention relates to a method for the improvement of current efficiency in electrolysis. According to the method, a theoretical cell voltage is first calculated, which is compared with the measured voltage. The cumulative difference between the theoretical and measured cell voltage is monitored constantly and when this difference is proportioned to current efficiency,
10 information on the status of the process can be obtained continually. A decrease in current efficiency is a clear indicator of short circuits between the electrodes, and by means of the method according to the invention, it is possible to concentrate the short circuit removal work into the correct cell groups, from the point of view of the current efficiency of the electrolysis.

15 In the electrolytic treatment of metals, the desired metal is deposited onto the surface of the electrode, the cathode. The treatment is carried out with the aid of an electric current in electrolysis cells, where a row of plate-like anodes and plate-like cathodes of electro conductive material are immersed
20 alternately into the liquid present, the electrolyte. The desired metal can be precipitated onto the cathode in the electrolytic treatment either by using soluble anodes of the same metal as that which is to be precipitated, or using insoluble anodes. Soluble anodes are used, for instance, in copper electrorefining and insoluble anodes are used, for example in the
25 electrowinning of nickel or zinc.

In the electrolytic refining of copper, the impure so-called anode copper is dissolved by means of electric current and the dissolved copper is reduced onto the cathode plate as very pure, so-called cathode copper. A sulfuric acid-based copper sulfate solution is used as the electrolyte. A copper starting sheet or so-called permanent cathode, can be used as the cathode plate at the beginning of the process, said permanent cathode can be made of acid-resistant steel or titanium. One, or several, rectifiers are used as the

current source in electrolysis. Current density of 250 – 320 A/m² is typically used, and the current is direct current (DC). Electrolysis takes place in separate electrolysis cells, where the number of anode-cathode pairs varies from plant to plant, being typically 30-60 pairs. There are varying numbers of 5 electrolytic cells in the different plants. Anodes are typically dissolved for 14 – 21 days, whereas the cathode cycle is 7 – 10 days.

The production capacity of an electrolysis plant is dependent upon the current intensity, the number of electrolytic cells and upon the time and 10 current efficiencies of the plant. The efficiencies describe how well temporally the cells in the plant are in use (current on) and how well the electric current is used for depositing the copper. The capacity of electrolysis plants is raised by increasing the current intensity applied, building more electrolytic cells or by improving the efficiencies.

15

Current efficiency is an essential parameter when examining the copper electrolysis process, its capacity and economic efficiency. The term tells the electric current proportion, which is applied for depositing copper onto the cathodes, compared with the theoretically calculated maximum amount of 20 deposit with that current. In practice the short circuits occurring between the anodes and cathodes decrease the current efficiency most drastically. In a short circuit the electric current travels directly from one electrode to another without depositing copper from the electrolyte. The electric current thus goes to waste.

25

In the prior art, in US patent 4,038, 162 a method is described for the prevention and removal of short circuits and thereby for the increase of current efficiency. The method is based on measuring the total current, for example with the aid of a magnetic field, after which an automatic cathode-replacing device is directed into position, which device replaces the short-circuited cathode for a new one.

Several different factors of the electrolysis process affect the occurrence of short circuits, such as current distribution, impurities in the electrolyte and the anode properties. Disturbances occurring in the process can easily be seen as an increase in short circuits. The number of short circuits in the day-to-day 5 electrolysis process can be considered a good indicator of the status of the process. At present, short circuits are observed and removed manually, which in practice means a tremendous amount of work every day.

According to this invention, a continuous method has been developed for the 10 improvement of current efficiency, whereby the cell voltage of the electrolysis cell groups is measured continually, which cell voltage is compared to the calculatory cell voltage, and the cumulative difference in voltages is proportioned to the current efficiency in order to concentrate the short circuit removal work on the cell groups having the lowest current efficiency. Thus 15 the method is based on the information from different measured data from the electrolysis process and on the utilization of this information. Upon implementation of the method, it is no longer necessary to manually go through each cell group separately, but work can be concentrated to the more critical cell groups and thus the current efficiency of the whole 20 electrolysis plant can be increased. The essential features of the invention are presented in the enclosed claims.

In the method developed, the theoretical cell voltage is first calculated on the basis of the process measurements and variables. The process 25 measurements used are temperature and composition of the electrolyte and used electric current. The variables are spacing between electrodes and number of cells between the cell voltage measuring points. When the theoretical cell voltage is compared to the measured voltage, it is possible to obtain information of the short circuit status of the cell group. In practice, it is 30 worthwhile to measure cell voltage in electrolysis per half-group, as anodes are generally changed by half group and the cell voltage also varies accordingly. By "cell group" below is also meant half groups or other entity,

where anodes are changed simultaneously. The greater the difference between measured and theoretical cell group voltage, the higher the number of short circuits in the group. Thus it is possible to obtain valuable additional information on the status of the cell groups for both process control and for

5 the control of short circuit removal work. When the work is concentrated to the critical cell groups, no damage is caused with needless inspection rounds of the cell groups that are running well. The general view of the short circuit status is also clearer than before.

10 For current efficiency forecasting purposes, a model is used which is composed of several cathode cycle series. From the series of measurement, for each cathode cycle a theoretical and measured cell voltage cumulative difference is calculated, which is proportioned to the current efficiency obtained. The results of tests performed have shown that the dependency

15 between the cumulative difference and the current efficiency achieved is quite linear. It has been observed that in practice the method forecasts the current efficiency to be achieved to an accuracy of $\pm 1\%$.

In practice, therefore, the cell voltage is measured as on-line type, in other words continuously in cell groups. From the difference between the theoretical and calculated cell voltage it is possible to deduce the current efficiency of the group or half group in question. Short circuits of the cell groups having the lowest current efficiency are worked out first. Thus it is possible to avoid disturbances to a well running group and to concentrate

20

25 only on the groups requiring immediate attention. By means of the method, it is possible to improve the current efficiency of the entire electrolysis plant compared to the traditional manual operation. Additionally, savings are made in labor costs.

PATENT CLAIMS

1. A method for the improvement of current efficiency in an electrolysis,
characterized in that with the aid of the measured variables from the
5 electrolysis process, the calculated theoretical cell voltage of the
electrolytic cells is continually compared with the measured real cell
voltage, and the cumulative difference in voltages is proportioned to the
current efficiency in order to concentrate the short circuit removal work in
the cell groups with the lowest current efficiency.
- 10 2. A method according to claim 1, **characterized in that** the temperature
and composition of the electrolyte, spacing between electrodes, number
of cells and electric current are the variables used for the calculation of
the theoretical cell voltage.
- 15 3. A method according to claim 1, **characterized in that** there is a linear
connection between the cumulative difference in the theoretical and
measured cell voltage and the current efficiency achieved.

20

25

30

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00522

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C25C 7/06, G01R 31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C25C, G01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3809902 A (DANIEL B. COFER ET AL), 7 May 1974 (07.05.74), column 5, line 5 - line 23; column 8, line 7 - line 14, figures 1-3, abstract --	1-3
A	US 3793166 A (FRANK D. SHAW), 19 February 1974 (19.02.74), abstract --	1-3
A	US 4038162 A (AARNE ALBIN KAPANEN ET AL), 26 July 1977 (26.07.77), abstract --	1-3
A	US 3574073 A (RICHARD W. RALSTON, JR.), 6 April 1971 (06.04.71), abstract --	1-3

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

26 Sept 2002

27-09-2002

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer

Ulrika Nilsson/ELY
Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00522**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3256172 A (JOHANNES DÖRFEL ET AL), 14 June 1966 (14.06.66) --- -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/09/02

International application No.

PCT/FI 02/00522

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 3809902 A	07/05/74	ES	421439 A	01/07/76
		FI	62600 B,C	30/09/82
		FR	2210770 A,B	12/07/74
		IT	1008587 B	30/11/76
		TR	18439 A	16/02/77

US 3793166 A	19/02/74	US	3652935 A	28/03/72
		US	3753104 A	14/08/73

US 4038162 A	26/07/77	CA	1061881 A	04/09/79
		DE	2614658 A,B,C	14/10/76
		FI	53463 B,C	31/01/78
		FI	751086 A	11/10/76
		GB	1505223 A	30/03/78
		JP	1049879 C	26/06/81
		JP	51124605 A	30/10/76
		JP	55040675 B	20/10/80

US 3574073 A	06/04/71	DE	1944051 A,B	26/03/70
		FR	2017393 A	22/05/70
		GB	1233679 A	26/05/71
		JP	48025319 B	27/07/73

US 3256172 A	14/06/66	DE	1173068 B	02/07/64
		GB	992020 A	12/05/65
